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# PATENT SPECIFICATION

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The Inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949, are:—HARRO PETERSEN, WILHELM RUEMENS, WILHELM RUETTIGER and ANTON FEINAUER, citizens of the Federal Republic of Germany, residing, respectively, at 17 Augusta-Anlage, Mannheim, 35 Hardenburgstrasse, Limburgerhof/Pfalz; 38 Rheinruhenstrasse, Ludwigshafen/Rhein; and 74 Hohenzollernstrasse, Ludwigshafen/Rhein; Federal Republic of Germany.

## COMPLETE SPECIFICATION

### Improving Cellulosic Fibrous Materials

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to a process for the crease-resist finishing of cellulosic fibrous materials (i.e. fibrous materials containing or consisting of cellulose) by reacting the fibrous material with a substance having a molecular weight of up to 350 containing at least one N-methylol group and/or N-methylol ether group in the presence of an acid catalyst and in the presence of trioxane.

It is known that cellulosic fibrous material may be improved by impregnating it with aqueous solutions or dispersions of low molecular weight substances which contain at least one N-methylol group and/or N-methylol ether group and of acid or potentially acid catalysts and then reacting the N-methylol groups and N-methylol ether groups with each other, with other groups of the substance bearing them, and/or with the cellulose.

The object of this treatment is above all to lessen the tendency of cellulose to crease. Reaction with the N-methylol groups and N-methylol ether groups is usually carried out by drying the impregnated material and heating it to a temperature of up to 160° C. Dry crease angles and wet crease angles are thus obtained which are in the same order of magnitude. The size of the angles could be adapted to all requirements were it not for the fact that the tensile strength of the treated material decreases the greater the dry crease angle is made.

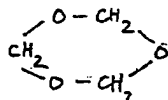
It has therefore already been recommended that the above-mentioned reaction be carried out on the swollen fibrous material without drying. While in this way it is possible to achieve a marked increase in the wet crease angle without excessive loss of tensile strength, the dry crease angle is not improved and satisfactory behaviour of the treated material in use is not ensured.

According to more recent knowledge, optimum results are achieved when a great wet crease angle and a medium great dry crease angle are imparted to the fibrous material with only slight damage to the fiber. To achieve this result it has hitherto been necessary to carry out a finishing in the swollen condition and a finishing in the dry condition in a two stage process. Attempts have already been made to achieve

similar results in a one stage process by treating the fibrous material with formaldehyde and careful drying at low temperatures, but this method is so difficult to control that reproducible effects cannot be obtained with certainty. A simple single stage process for achieving great wet crease angles and medium great dry crease angles which is reliable in operation has hitherto been lacking.

It is an object of this invention to finish cellulosic fibrous material (i.e. fibrous material containing or consisting of cellulose) in a particularly simple and reproducible manner so that it acquires a great wet crease angle and a medium great dry crease angle. Another object of the invention is to carry out such a process in a single operation. Furthermore it is an object of the invention to provide fibrous material with the said properties without unduly decreasing the tensile strength.

These objects are achieved in accordance with this invention by impregnating cellulosic fibrous material with an aqueous solution or dispersion of a substance having a molecular weight of up to 350 which contains at least one N-methylol group and/or N-methylol ether group and with an aqueous solution or dispersion of an acid catalyst, and reacting the N-methylol groups and N-methylol ether groups with each other, with other groups of the substances bearing them and/or with the cellulosic material in the presence of trioxane of the formula



in an amount of 0.1 to 4 times the total molar amount present of these groups.

The term acid catalyst as used herein is meant to include potentially acid catalysts which act as acids under the curing conditions.

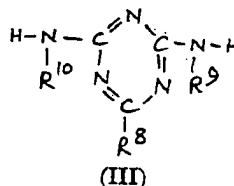
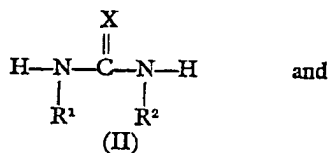
The fibrous material for the present process may be fibrous structures such as threads, filaments, fibers, bands, bonded and unbonded non-woven fabrics, knitted fabric, netting and particularly woven fabric consisting of natural or regenerated cellulose fibers, for example of cotton, linen, viscose staple fiber or rayon, or containing the same together with other fibers, such as wool, silk, cellulose ester fibers or fibers of acrylonitrile polymers, linear polyamides, linear polyesters or polyolefins.

Substances bearing N-methylol groups and/or N-methylol ether groups and having a molecular weight of up to 350 contain at least one group and preferably at least two groups having the formula:—



in which R denotes a hydrogen atom or an alkyl radical preferably having one to five carbon atoms.

The most important and most widely used substances of this type are derived from parent substances having urea or triazine structure which may be represented by the following general formulae:—



In formula II, X denotes a sulfur atom or preferably an oxygen atom, R<sup>1</sup> and R<sup>2</sup> (which may be identical or different) denote alkyl radicals having one to five carbon atoms or preferably hydrogen atoms or radicals having the formula:—



which are connected together direct or via radicals having the formula



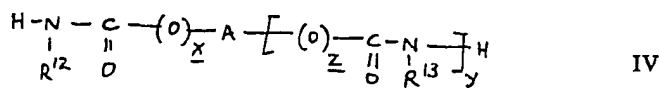
or —O— or —N—R<sup>7</sup>, R<sup>3</sup> denotes an alkyl radical having one to five carbon atoms, an aryl radical or preferably a hydrogen atom, R<sup>4</sup> denotes an alkyl group having one to five carbon atoms or preferably a hydrogen atom, a hydroxy group or an alkoxy

group having one to five carbon atoms or, if the two  $R^3-C-R^4$  groups are connected together direct, both  $R^4$  groups together may form the radical  $-NH-C-NH-$ , 5

R<sup>3</sup> denotes an alkyl radical having one to five carbon atoms or preferably a hydrogen atom, R<sup>4</sup> denotes an alkoxy group having one to five carbon atoms or preferably a hydrogen atom or a hydroxy group and R<sup>1</sup> denotes a hydrogen atom or an alkyl or hydroxyalkyl radical having one to five carbon atoms.

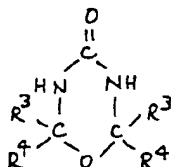
10 In formula III,  $R^8$  denotes a hydrogen atom, an alkyl group having one to five carbon atoms or a radical having the formula  $-\text{NH}-R^{11}$  and  $R^9$ ,  $R^{10}$  and  $R^{11}$  (which may be identical or different) denote alkyl groups having one to five carbon atoms or preferably hydrogen atoms. 10

15 Another group of parent substances whose N-methylol and N-methylol ether derivatives are of importance for improving cellulosic fibrous material have the general formula: — 15

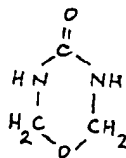


20 In this formula,  $R^{12}$  and  $R^{13}$  (which may be identical or different) denote hydrogen atoms or alkyl radicals having one to five carbon atoms, A denotes a divalent, preferably aliphatic, hydrocarbon radical having two to eight carbon atoms,  $x$  denotes zero or 1,  $y$  denotes zero or 1,  $z$  denotes zero or 1,  $x$  and  $z$  preferably being identical, and the sum of  $(x+y)$  is 1 or 2. 20

Substances having the formula II include monoalkylureas and N,N'-dialkylureas, such as N-methylurea, N-butylurea, N,N'-diethylurea, N-methyl-N'-amylurea and the corresponding thioureas, and particularly urea, N,N'-ethylenurea (=imidazolidone-2), N,N'-1,2-propylenurea (=4-methylimidazolidone-2), N,N'-1,3-propylenurea (=N,N'-trimethylenurea or hexahydropyrimidone-2), 5-hydroxy-hexahydropyrimidone-2, hexahydro-1,3,5-triazinone-2 and its 5-alkyl and 5-hydroxy-alkyl derivatives, e.g. 5-isobutyl-hexahydro-1,3,5-triazinone-2, glyoxalmonoureine (=4,5-dihydroxyimidazolidone-2), acetylenediurea (=glyoxaldiureine) and urones of the formula



where R<sup>3</sup> and R<sup>4</sup> have the meanings mentioned above, e.g. unsubstituted urone of the formula



Examples of substances having the formula III are N-monoalkylmelamines, N,N'-dialkylmelamines, N,N',N''-trialkylmelamines, acetoguanamine (= 2,4-diamino-6-methyl-1,3,5-triazine) and particularly melamine.

Examples of substances having the formula IV are dicarboxylic diamides, such

as adipic diamide and succinic di-(methylamide), and particularly monocarbamic and dicarbamic esters (=monourethanes and diurethanes), such as ethyl carbamate (= urethane in the narrow sense, or ethyl urethane), propyl carbamate, butyl carbamate, octyl carbamate, ethyl N-methylcarbamate, butyl N-ethylcarbamate, dicarbamic esters and di-N-ethyl-carbamic esters of ethylene glycol, 1,3-butanediol, 1,4-butanediol and 1,6-hexanediol. Of special technical interest are ethyl urethane and butanediol-1,4-urethane.

Acid catalysts, which term is meant to include potentially acid catalysts, i.e. compounds which act as acids under the curing conditions, are generally known and conventional for the purpose of crease resist finishing. Examples are inorganic and organic acids, such as sulfuric acid, hydrochloric acid, phosphoric acid, boric acid, formic acid, acetic acid, tartaric acid and salts having an acid reaction or forming acids by the action of heat or hydrolysis, for example ammonium salts or strong and medium strength acids, such as ammonium sulfate, ammonium chloride, ammonium phosphates, ammonium nitrate, ammonium acetate and ammonium citrate, amine salts, such as dimonoethanolamine hydrogen phosphate and ethanolamine hydrochloride, and metal salts of strong acids, such as magnesium chloride, aluminum chloride, zinc chloride and zinc nitrate. The substances of the said type may be used as catalysts individually or mixed together.

The substances containing at least one N-methylol group and/or N-methylol ether group and the acid catalysts are applied to the material to be treated by conventional methods, for example by dipping, spraying or other impregnation methods. The substances containing N-methylol groups and/or N-methylol ether groups may be applied in amounts of 3 to 12% by weight on the weight of the dry material to be treated. The catalysts are preferably used at the rate of 3 to 20% by weight on the methylol compounds or methylol ether compounds used. The N-methylol groups and/or N-methylol ether groups are then allowed, also in a conventional manner, to react with each other, with other groups of the substances bearing them and/or with the cellulose. For the success of the present process it is essential that the said reaction (curing) be carried out in the presence of 0.1 to 4 times, preferably 0.2 to 2 times, the molar amount of trioxane, with reference to the N-methylol groups and N-methylol ether groups. This may be effected for example by applying a solution of trioxane to the material to be treated (impregnated as described above) prior to the commencement of the reaction. It is preferable however to impregnate the material to be treated with an aqueous liquor which contains at the same time (a) one or more substances having a molecular weight of up to 350 and containing N-methylol groups and/or N-methylol ether groups, (b) an acid or potentially acid catalyst and (c) the necessary amount of trioxane.

Reaction of the N-methylol groups and N-methylol ether groups is preferably carried out by drying the impregnated fibrous material and then heating it to a temperature of up to 180° C., preferably 130° to 160° C. Under these conditions the reaction is usually over in one to six minutes.

In a particular embodiment of the process, the fibrous material may be mechanically shaped during the drying or thereafter, for example by compression, crimping, goffering, ironing, calendering, embossing or pleating. After reaction of the N-methylol groups and N-methylol ether groups, the shape imparted to the fibrous material is resistant to washing. The treated material may then be washed, rinsed and dried in the conventional manner.

There is moreover the very advantageous possibility of drying the fibrous material at elevated temperature, preferably at about 120° C., after impregnation and then maintaining the material at a temperature of about 60° C. for reaction of the N-methylol groups and N-methylol ether groups, preferably for four to ten hours. The material thus treated may then be washed in an alkaline liquor, rinsed and dried in the usual way.

In many cases it is advantageous to add to the impregnation liquor (which contains the compound bearing N-methylol groups and/or N-methylol ether groups, the catalyst and trioxane) a wetting agent and/or conventional treatment agents for fibrous materials, for example water-repellent agents, plasticizing agents and finishes. Examples of wetting agents are salts of alkyl-naphthalene sulfonic acids and the alkali metal salts of sulfonated dioctyl succinate. Water-repellent agents are for example the known paraffin wax emulsions containing aluminum or zirconium, and also preparations containing silicones and perfluorinated aliphatic compounds. Examples of plasticizing agents are ethenoxylation products of high molecular weight fatty acids, fatty alcohols or fatty acid amides, high molecular weight polyglycol ethers and esters thereof, high

molecular weight fatty acids, fatty alcohol sulfonates, stearyl-N,N-ethylenurea and stearylaminomethylpyridinium chloride. Examples of finishing agents are cellulose ethers, cellulose esters and alginates, and also solutions or dispersions of synthetic polymers, for example polyamides, polyvinyl ethers, polyvinyl alcohols, polyacrylic acid or esters and amides thereof and also the corresponding polymethacrylic compounds, polyvinyl propionate, polyvinyl pyrrolidone, copolymers, for example those of vinyl chloride and acrylic esters, butadiene and styrene or acrylonitrile, or those of  $\alpha$ -dichloroethylene,  $\beta$ -chloroalkylacrylic esters or vinyl- $\beta$ -ethyl ethers and acrylamide or the amides of crotonic acid or maleic acid or of N-methylolmethacrylamide and other polymerizable compounds. Isocyanates, diisocyanates, polyethylenimines, polyamines, ethenoxylated polyamides or silicic esters may also be added to the impregnation liquors.

It is also possible to add dyes and levelling agents to the impregnation liquors in order to dye the fibrous material and give it a crease-resist finish in one operation. Water-soluble metal complex dyes have proved to be particularly suitable for this purpose; such dyes are described in British Patent Specifications Nos. 692,073, 747,367, 766,402, 793,136, 667,168, 684,646 and 787,843. Dyes which are particularly suitable for the process according to this invention include quite generally azo compounds which contain metals, such as chromium, cobalt and copper, combined therein and which are suitable for dyeing wool. Dyes of this kind are well known to the art and are listed for example in the Colour Index (1956) under "acid dyes". The dyes should be contained in the impregnating liquor at the most in the same amount by weight as the substance containing N-methylol groups and/or N-methylol ether groups.

The process according to the present invention permits the finishing in a simple and reliable manner and in a single operation of cellulosic fibrous material so that it has great to very great wet crease angles and medium great dry crease angles. By varying the molar ratio of trioxane to N-methylol groups and/or N-methylol ether groups, it is possible to adapt the level of, and difference between, the wet and dry crease angles to the requirements in each individual case. If the process is carried out with a prolonged treatment at a temperature of about 60° C., it is possible to achieve particularly good abrasion resistance and tensile strength of the material being treated, in addition to the advantages mentioned above.

The invention is further illustrated by the following Examples in which parts and percentages are by weight.

#### EXAMPLE 1.

A bleached mercerized cotton cloth (poplin) is impregnated on a padding machine with an aqueous liquor which contains in 1000 parts 60 parts of a 50% solution of N,N'-dimethylolurone dimethyl ether, 80 parts of trioxane, 30 parts of a 40% polymer dispersion prepared as described below, 3 parts of a reaction product of 1 mole of isooctylphenol and 3 moles of ethylene oxide, 40 parts of a 50% aqueous solution of an ethenoxylated polyamide and 30 parts of magnesium chloride to a liquor retention of 70%, dried on a stenter and condensed for four minutes at 160° C. It is also possible to compress the cloth prior to condensation. Following condensation there is carried out either an alkaline wash or a treatment with plasticizing agents or smoothing agents, depending on the handle desired.

The following crease angles are determined:

	warp	weft
dry crease angle after unloading for sixty minutes according to DIN 53,890	105	107
wet crease angle according to Tootal	135	140.
(British Patent Specification No. 727,890, page 5, lines 98—116)		

The polymer dispersion used is prepared as follows:—

5 parts of methylolmethacrylamide (dissolved in 95 parts of butyl acrylate) is mixed while stirring with a solution of 1 part of potassium persulfate and 2 parts of the sodium salt of a paraffinsulfonic acid ( $C_{12}$  to  $C_{18}$ ) in 500 parts of water. While stirring at 80° C. a solution of 15 parts of methylolmethacrylamide in 285 parts of butyl acrylate and 3 parts of potassium persulfate and 6 parts of the sodium salt of a paraffinsulfonic acid ( $C_{12}$  to  $C_{18}$ ) in 100 parts of water are allowed to flow in during the course of about forty-five minutes. The whole is then held at a temperature of 80° to 90° for about an hour. During the polymerization, the pH value falls from 6.5

prior to polymerization to 3.5 measured after the polymerization. A stable non-coagulating dispersion is thus obtained.

#### EXAMPLE 2.

A printed cotton cloth is impregnated to a liquor take-up of 75% on a padding machine with an aqueous liquor containing in 1000 parts 55 parts of a 50% solution of dimethylolpropyleneurea, 85 parts of trioxane and 50 parts of magnesium chloride, dried on a pin stenter at 120° C. and condensed for four minutes at 160° C. The cloth is then washed in an alkaline liquor with 2 g/l of sodium carbonate and 5 g/l of soap and if desired treated with a plasticizer according to the desired handle. The following dry and wet crease angles are obtained:—

	<i>warp</i>	<i>weft</i>
dry crease angle after unloading for sixty minutes according to DIN 53,890	97	101
wet crease angle according to Tootal	132	137.

#### EXAMPLE 3.

A viscose staple fiber fabric is impregnated to a liquor take-up of 88% on a padding machine with an aqueous liquor containing in 1000 parts 180 parts of a 70% aqueous paste of N,N'-dimethylolurea dimethyl ether, 100 parts of trioxane, 30 parts of a 20% aqueous solution of a copolymer of equal parts of acrylamide and methacrylamide, 10 parts of a 30% aqueous solution of an ester, reacted with dimethyl sulfate, of equimolar amounts of stearic acid and triethanolamine, and 15 parts of zinc chloride, dried on a pin stenter and heated for four minutes at 150° C. After the heat treatment the fabric is washed in an alkaline liquor in conventional manner.

The following crease angles are determined:—

	<i>warp</i>	<i>weft</i>
dry (DIN 53,890)	94	96
wet (Tootal)	124	128.

#### EXAMPLE 4.

A viscose staple fiber fabric is impregnated to a liquor take-up of 87% on a padding machine with an aqueous liquor containing in 1000 parts 100 parts of a 50% aqueous solution of N,N'-dimethylolbutanediol-1,4-diurethane, 50 parts of trioxane, 5 parts of a 50% aqueous dispersion of polyvinylmethyl ether, 3 parts of polyethylene oxide having a mean molecular weight of 3,000, 15 parts of a 40% aqueous paste of an adduct of 2.6 moles of ethylene oxide to 1 mole of stearic acid ethanolamide and 5 parts of ammonium nitrate. The fabric is dried on a stenter, heated for four minutes at 160° C. and then washed in an alkaline liquor in conventional manner.

The fabric thus finished has the following crease angles:—

	<i>warp</i>	<i>weft</i>
dry	95	100
wet	134	141.

#### EXAMPLE 5.

A bleached and mercerized cotton fabric (shirting poplin) is impregnated to a liquor take-up of 83% on a padding machine with an aqueous liquor containing in 1000 parts 120 parts of a 50% aqueous solution of dimethylol ethyl carbamate, 60 parts of trioxane and 45 parts of magnesium chloride hexahydrate. The impregnated fabric is dried on a stenter, heated for four minutes at 160° C. and washed in an alkaline liquor in conventional manner.

The fabric has the following crease angles:—

	<i>warp</i>	<i>weft</i>
dry	108	128
wet	123	141.

#### EXAMPLE 6.

A bleached and mercerized cotton fabric is impregnated with an aqueous liquor containing in 1000 parts 100 parts of a 50% aqueous solution of 5-isobutyl-1,3-dimethylolhexahydrotriazinone-(2), 150 parts of trioxane and 20 parts of manganese

chloride hexahydrate. The liquor take-up is 80%. The fabric is dried on a stenter and heated for four minutes at 160° C.

The fabric has the following crease angles:—

5	dry	<i>warp</i>	<i>weft</i>	5
	wet	105	109	
		120	139.	

#### EXAMPLE 7.

A bleached and mercerized cotton imitation poplin is impregnated with an aqueous liquor containing in 1000 parts 100 parts of a 60% aqueous solution of highly methylolated melamine partly etherified with methanol, 85 parts of trioxane and 20 parts of magnesium chloride hexahydrate. The liquor take-up is 78%. The fabric is dried on a stenter, heated for four minutes at 155° C. and then washed in an alkaline liquor.

The fabric has the following crease angles:—

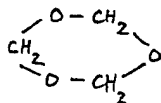
15	dry	<i>warp</i>	<i>weft</i>	15
	wet	107	123	
		119	130.	

#### EXAMPLE 8.

A bleached and mercerized cotton imitation poplin is impregnated on a padding machine with an aqueous liquor containing in 1000 parts 100 parts of a 50% aqueous solution of dimethylolglyoxal monoureine, 100 parts of trioxane, 40 parts of a 40% aqueous dispersion of an *n*-butyl acrylate polymer containing small amounts of *N*-methylolmethacrylamide units, 2 parts of an adduct of 7 moles of ethylene oxide to 1 mole of isocetylphenol, 2 parts of the dye C.I. Acid Blue 158 and 5 parts of ammonium chloride. The liquor take-up is 81%. The fabric is dried on a stenter to a residual moisture content of 10%, embossed on a calender at 190° C. and heated for four minutes at 150° C. An embossed and dyed fabric is obtained whose embossed effect and color are resistant under the conditions of washing c, DIN 54,011.

#### WHAT WE CLAIM IS:—

1. A process for improving cellulosic fibrous material, which comprises impregnating the material with an aqueous solution or dispersion of a substance having a molecular weight of up to 350 containing at least one *N*-methylol group and/or *N*-methylol ether group, and with an aqueous solution or dispersion of an acid catalyst, and reacting the *N*-methylol groups and *N*-methylol ether groups with each other, with other groups of the substances bearing them and/or with the cellulosic material, in the presence of trioxane of the formula



- in an amount of 0.1 to 4 times the total molar amount present of the *N*-methylol groups and *N*-methylol ether groups.
2. A process as claimed in claim 1 wherein the reaction of the *N*-methylol groups and *N*-methylol ether groups is carried out by drying the impregnated fibrous material and heating it to a temperature of up to 180° C.
3. A process as claimed in claim 2 wherein the fibrous material is shaped mechanically during the drying.
4. A process as claimed in any of claims 1 to 3 wherein reaction of the *N*-methylol groups and *N*-methylol ether groups is carried out by drying the impregnated fibrous material at elevated temperature and allowing the dried material to remain at a temperature of about 60° C.
5. A process as claimed in any of claims 1 to 4 wherein a wetting agent and/or one or more conventional agents for treating fibrous materials is added to the impregnation liquor.
6. A process as claimed in any of claims 1 to 5 wherein a metal complex dye is added to the impregnation liquor.
7. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

8. Cellulosic fibrous material which as been improved by the process claimed in any of claims 1 to 7.

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